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The high-performance, cost-effective computing provided by massively parallel computers can be expected to have a significant impact on our ability to simulate complex physical and engineering systems. Such capabilities will strengthen the competitiveness of U.S. defense and commercial industries. However, robust simulations of systems such as flowfields over hardbodies and plumes must increasingly rely on an adequate data base for the fundamental chemical and physical processes occurring in these systems. Much of this data base is either unavailable or experimentally inaccessible.

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Electron-Molecule Collisions and UV Signatures in Flowfields

Final Technical Report

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I. *Background*

Electrons produced by various ionization processes can play an important role in determining spectral radiative intensities and other characteristics of hardbody flowfields and rocket plumes. Robust modelling of the radiation emitted from such flows, as well as of other physical and chemical properties, must include collisional processes involving these low-energy electrons with the molecular species present. Although the collision energies are low, non-equilibrium behavior in hardbody flowfields can lead to overshoots resulting in temperatures in the 12,000 K range. Electrons in the tail of these energy distributions can, and are believed to, cause electronic excitation of species in these flowfields. Cross sections for such threshold excitation by electrons with just sufficient energy to drive the process are generally inaccessible experimentally and the data base of these cross sections is essentially nonexistent. Furthermore, impact of very low-energy electrons, present in relatively high number densities in these low-temperature plasmas, on electronically excited metastable states can lead to significant depopulation of these states. Very little is known about such cross sections for electron impact on metastable states other than they are expected to be quite large.

In summary, many of the cross sections for electron-molecule collisions needed for robust modelling of the properties of hot interacting flow fields associated with hardbodies and plumes, such as radiative signatures, are not known. Use of unreliable or guessed values of these cross sections can lead to incorrect models of the underlying processes responsible for radiative signatures and their behavior with velocity and altitude. Models based on such unreliable cross sections can fail seriously outside of the limited range where some validation may have been apparent.

One strategy for obtaining these cross sections, particularly those which are experimentally inaccessible, is to calculate them. The major hindrance to such a strategy, however, has been the huge computational demands associated with the solution of the equations governing electron-molecule collisions at low impact energies. In fact, it is widely recognized

that the cost-to-performance ratio of conventional vector supercomputers such as the CRAY Y-MP has made such an approach impractical.

II. *Technical Summary*

A. *Objective*

The objective of this effort was to exploit a theoretical formulation and computational methodology which we have specifically developed for such applications to calculate the cross sections for electron impact excitation of molecules such as N_2, O_2, NO, OH, CN, and H_2O. These cross sections are needed for robust modelling of the ultraviolet emission occurring in the bow shock of a ballistic missile. Such ultraviolet signatures have a clear potential for detection and tracking of ballistic and theater missiles. The calculation of these cross sections for molecules is a computationally intensive quantum-mechanical problem. These computational demands and complexities have severely limited progress in such studies to date. As we will see shortly, one of our key accomplishments has been our ability to successfully exploit the high-performance and cost-effective computing provided by massively parallel supercomputers to meet the computational demands of these calculations. These parallel supercomputers achieve very high aggregate speeds and large memory by harnessing the power of commercially available microprocessors assembled in a scalable architecture. Such parallel computers can be expected to revolutionize our ability to model complex physical and chemical systems.

B. *Summary of Accomplishment*

(a) *Background*

To put our accomplishments in perspective it is essential to review a few salient features of our formulation of the electron-molecule collision problem and the computational methodology used in these studies. As in many complex physical systems, we do not attempt to

integrate the relevant wave equation governing these collisions but, instead, employ a variational principle which reduces the problem to one of solving systems of linear equations for the quantity of direct physical interest. In these applications this quantity is the scattering amplitude from which the cross section is determined. We use a multichannel extension of the variational principle for the scattering amplitude originally introduced by Schwinger.[1] This Schwinger multichannel variational procedure was specifically formulated for applications to electron-molecule collisions.[2] A key feature of this multichannel variational procedure is that, as in the original Schwinger principle, the trial wave function need not satisfy scattering boundary conditions; in particular, square-integrable functions such as Cartesian Gaussians, commonly used in molecular electronic structure calculations, may be employed.

Use of this variational principle leads to a system of linear equations

$$\mathbf{A}\,\mathbf{x} = \mathbf{b}, \tag{1}$$

whose solutions x yield the scattering amplitude. In Eq. (1) A is a complex symmetric matrix and b and x are rectangular complex matrices. The elements of the matrices A and b have the form

$$A_{ij} = \langle \phi_i | \left(\frac{1}{N+1} - P \right) \hat{H} + VP - VG_P^{(+)} V | \phi_j \rangle \tag{2}$$

and

$$b_{im} = \langle \phi_i | V | \Phi_m(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) \exp(i\mathbf{k}_m \cdot \mathbf{r}_{N+1}) \rangle . \tag{3}$$

In Eq. (2) ϕ_i and ϕ_j are (N + 1)-electron Slater determinants in which the trial scattering wave function for the composite system of electron plus molecule is expanded, $\hat{H} = E - H$, where H is the Hamiltonian for the incident electron plus molecular target with N electrons, V is the potential energy operator for the interaction of the incident electron with the target, P is a projection operator which selects open channels (energetically allowed outcomes of the collision), and $G_P^{(+)}$ is the interaction-free Green's function with appropriate boundary

conditions, projected onto the open channels. In Eq. (3) Φ_m is an eigenstate of the molecular target with energy E_m and exp $(ik_m \cdot r_{N+1})$ describes a plane wave propagating in the direction given by k_m. The angle brackets in Eqs. (2) and (3) indicate integration over the coordinates of all electrons.

Construction of the matrices A and b requires the evaluation of several different types of integrals. The difficulty or ease of evaluation of the matrix elements arising in a variational principle is clearly a major factor in the choice of method. In our variational principle the trial wave function, i.e., the ϕ_i and ϕ_j of Eqs. (2) and (3), need not satisfy scattering boundary conditions. In fact, if we exploit this flexibility and expand the molecular orbitals in the Slater determinants ϕ_i, ϕ_j, and Φ_m in Cartesian Gaussian functions of the form

$$\alpha(r;\ell,m,n,R,\zeta) = N_\alpha (x-X)^\ell (y-Y)^m (z-Z)^n \exp(-\zeta |r-R|^2), \qquad (4)$$

where N_α is a normalization constant and R = (X,Y,Z), all integrals associated with the Hamiltonian (H) and potential (V) terms in Eqs. (2) and (3) can be evaluated analytically. Efficient techniques and algorithms have been developed for their evaluation. However, the integrals involving $VG_p^{(+)}V$ have no known analytic form and are by far the most difficult and computationally intensive. Quadrature of some form must be employed to evaluate these terms.

(b) *Computational Breakthrough*

The occurrence of terms containing the Green's function in variational principles based on integral equations has often discouraged their use, in spite of known benefits of these methods such as the flexibility of using trial functions which do not satisfy scattering boundary conditions and their favorable convergence.[3] A significant accomplishment of our work has been the development of a strategy for evaluation of these Green's function matrix elements on parallel computers consisting of hundreds of commercially available microprocessors. This strategy has

been successfully implemented on the Intel Touchstone Delta System, a multicomputer containing 512 Intel *i*860 microprocessors. Runs to date on the Intel Delta show sustained performance of several billions of arithmetic operations per second (Gigaflops) in calculations of the cross sections of interest to us. This performance far exceeds that seen on conventional supercomputers such as the CRAY Y-MP by more than a factor of 100 and, with increasing microprocessor speeds and scaling of these systems, can be expected to increase significantly in the near future. *This development opens up entirely new vistas in computational studies of this kind and, in fact, is an early indication of the revolutionary impact that scalable high-performance computing can be expected to have on our ability to model complex physical systems.*

In our quadrature of these matrix elements involving $VG_p^{(+)}V$, the principal step is the evaluation and subsequent transformation of a large number, e.g., 10^9 or 10^{10}, of two-electron integrals of the form

$$\int d^3r_1 \int d^3r_2 \alpha(r_1) b(r_1) \frac{1}{r_{12}} \gamma(r_2) exp(ik \cdot r_2), \qquad (5)$$

involving three Cartesian Gaussian functions (α, β, and γ) and a plane wave exp (ik·r). Although these integrals can be evaluated analytically via a few thousand lines of Fortran, their evaluation can be computationally demanding because the number of such integrals is large.

These two computationally intensive tasks (*i*) the evaluation of a very large number of elementary integrals describing the interaction between electrons, and (*ii*) the transformation of these elementary integrals into the many-electron integrals appearing in the variational expression, are ideally suited for implementation on distributed-memory parallel computers. These machines consists of fairly powerful commercially available microprocessors with substantial memory which operate autonomously and communicate with each other via a message-passing network. The evaluation of the large sets of two-electron integrals is readily parallelized: one simply has each microprocessor independently calculate a different subset of integrals. Such a parallel strategy is especially appealing since the integral-evaluation algorithms

involve recursive steps that make vectorization on sequential supercomputers difficult. The transformation of these integrals can be organized as a series of large distributed matrix multiplications between the global array of integrals stored in the microprocessors and a distributed transformation matrix that is easy to construct. Since there are generally too many integrals to hold in memory simultaneously, we treat γ and the magnitude of **k** in (5) as sequential indices. The relative importance of these two tasks depends on the problem at hand, but performance in each step far exceeds that achieved by the original, sequential program. A large production run on the full Intel Delta can sustain throughput of about 2.5 GFLOPS, *approximately 100 times the performance of the original sequential program on the* CRAY Y-MP.

(c) *Most Significant Results*

We have exploited this parallel computational procedure and processor time on the Intel Delta System to carry out some of the first robust calculations of the cross sections for excitation of the low-lying excited states of N_2, CO, H_2O, and other molecules by electrons with impact energies close to threshold. Although this threshold excitation region is most relevant in the modelling of these flowfields, it is also generally not accessible experimentally.

Our calculated cross sections for excitation of the $A\,^3\Sigma_u$ state, the lowest-lying metastable state of N_2 with a lifetime of ~1 sec., show a rapid onset at threshold and agree well with the single set of measured values which are available at a few electron volts above threshold.[4] No measured values are available closer to threshold. Due to its very long lifetime this metastable state plays an important role in modelling the radiative signatures from flowfields. For convenience, these cross sections are shown in the attached figure. Our calculated values provide the most reliable estimates of the cross sections for excitation of the $A\,^3\Sigma_u$ state of N_2 by electron impact at near-threshold energies. Cross sections for electron impact excitation of many other low-lying excited states of N_2 have also been calculated.

Agreement with measured values of these cross sections is quite encouraging in spite of the significant inconsistencies among the different data sets.

Similar calculations have been carried out for the cross sections for electron impact excitation of the lowest lying metastable $a\,^3\Pi$ state of CO which is the upper level of the Cameron bands of CO.[5] The cross sections also show a very rapid onset at threshold in agreement with values obtained from trapped electron measurements of thirty years ago.[6] Due to well-known difficulties associated with the technique, trapped electron measurements were not generally viewed as reliable. Cross sections for electron impact excitation of many other low-lying excited states of CO have also been calculated.[5] These calculations are being extended to obtain the cross sections for excitation of the $a\,^3\Pi$ state of CO via electron impact on high vibrational levels of the ground state. These cross sections could play a significant role in modelling systems with substantial populations of molecules in high vibrational levels.

We have also completed calculations of the cross sections for excitation of the $B\,^3\Pi_g$ state of N_2 by electron impact on the metastable $A\,^3\Sigma_u^+$ state. Electron impact on metastable states can lead to significant depopulation of excited electronic states in the low-temperature plasmas occurring in flowfields. The small energy gaps between excited electronic states, the high density of such excited states, and the larger number densities of electrons with sufficient energy to drive such excitations all contribute to the importance of this mechanism. To our knowledge, these calculations provide the only available estimates of cross sections for electron impact excitation of metastable molecular nitrogen. Further studies along these lines are under way for N_2 and CO.

We have also exploited our formulation and computational procedure to obtain cross sections for excitation and dissociation of H_2O by electron impact, i.e., $e + H_2O \rightarrow H + OH$. At the time of publication, these were the first results of ab initio calculations of such cross sections for a polyatomic molecule. Estimates of the cross section for electron impact dissociation of water based on the results of these calculations differ dramatically from the recommended values available in the literature.[7]

(d) *Summary and Outlook*

The high-performance, cost-effective computing provided by massively parallel computers can be expected to have a significant impact on our ability to simulate complex physical and engineering systems. Such capabilities will strengthen the competitiveness of U.S. defense and commercial industries. However, robust simulations of systems such as flowfields over hardbodies and plumes must increasingly rely on an adequate data base for the fundamental chemical and physical processes occurring in these systems. Much of this data base is either unavailable or experimentally inaccessible.

Our use of parallel computers in these studies of electron collisions with molecules for modelling of flowfields is an early example of the significant role that scalable high-performance computing can play in meeting such data-base needs for several defense and dual-use applications. With the projected scaling of these machines to much larger numbers of microprocessors and improvements in hardware and algorithms, performance levels well in excess of that achieved on the early versions of the machines used in these studies can be expected. In summary, these machines will certainly have a revolutionary impact on our ability to model complex systems.

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III. *Publications resulting from the research outlined above include*

Cross Sections for Excitation of the $b\,^3\Sigma_u^+$, $a\,^3\Sigma_g^+$, and $c\,^3\Pi_u$ *States of* H_2 *by Low-Energy Electrons*
M.A.P. Lima, T.L. Gibson, V. McKoy, and W.M. Huo
Phys. Rev. A 38, 4527 (1988)

Studies of Elastic e-NH_3 *Collisions*
H.P. Pritchard, M.A.P. Lima, and V. McKoy
Phys. Rev. A 39, 2392 (1989)

Applications of the Schwinger Multichannel Method to Electron-Molecule Collisions
M.A.P. Lima, L.M. Brescansin, A.J.R. Silva, C. Winstead, and V. McKoy
Phys. Rev. A 41, 327 (1990)

Electronic Excitation of H_2O *by Low-Energy Electron Impact*
H.P. Pritchard, V. McKoy, and M.A.P. Lima
Phys. Rev. A 41, 546 (1990)

Studies of Electron-Molecule Collisions on the Mark IIIfp Hypercube
P. Hipes, C. Winstead, M. Lima, and V. McKoy
Proceedings of the Fifth Distributed-Memory Computing Conference,
Vol. I: Applications, edited by D.W. Walker and Q.F. Stout
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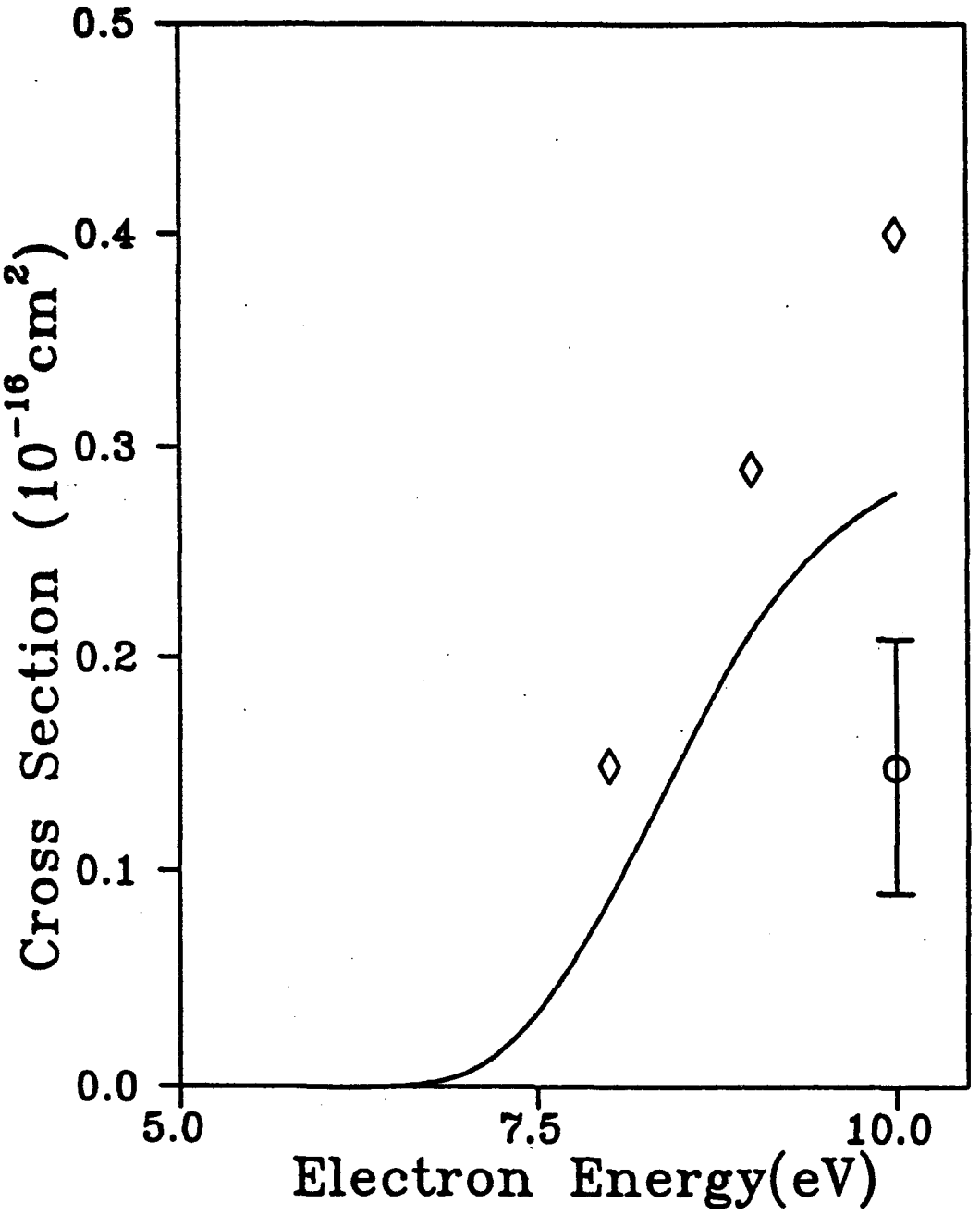
Studies of Electron Collisions with Polyatomic Molecules Using Distributed-Memory Parallel Computers
C. Winstead, P.G. Hipes, M.A.P. Lima, and V. McKoy
J. Chem. Phys. 94, 5455 (1991)

Electronic Excitation of Carbon Monoxide by Low-Energy Electron Impact
Q. Sun, C. Winstead, and V. McKoy
Phys. Rev. A1 46, 6987 (1992)

Application of the Schwinger Multichannel Method to Electronic Excitation of N_2 by Electron Impact
H.P. Pritchard, C. Winstead, V. McKoy, and M.A.P. Lima
Phys. Rev. A (submitted for publication)



- Cross section for electron impact excitation of the long-lived $A\,^3\Sigma_u^+$ state of N_2 : ——, present results ; Φ, value derived from measured differential cross sections (S. Trajmar et al., Phys. Rev. **A16**, 1013 (1977)) ; ◊, values derived from metastable detection (W. L. Borst, Phys. Rev. **A5**, 648 (1972)).